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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C04B 28/34, 20/02, 40/06 // (C04B 28/34, 14:04, 22:00)	A1	(11) International Publication Number: WO 00/24690 (43) International Publication Date: 4 May 2000 (04.05.00)
(21) International Application Number: PCT/BE99/00130 (22) International Filing Date: 22 October 1999 (22.10.99) (30) Priority Data: 9823285.3 23 October 1998 (23.10.98) GB (71) Applicant (for all designated States except US): VRIJE UNIVERSITEIT BRUSSEL [BE/BE]; Pleinlaan 2, B-1050 Brussels (BE). (72) Inventors; and (75) Inventors/Applicants (for US only): WU, Xiao [CN/BE]; Avenue d'Auderghem 350, B-1040 Brussels (BE). GU, Junn [CN/BE]; Avenue d'Auderghem 350, B-1040 Brussels (BE). (74) Agents: SCHMITZ, Yvon et al.; Gevers & Vander Haeghen, Rue de Livourne 7, B-1060 Bruxelles (BE).		(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: IMPROVED CEMENT COMPOSITION		
(57) Abstract The present invention concerns the field of cement, and relates particularly to phosphate cements. According to one aspect of the present invention there is provided a phosphate cement composition which comprises, in combination, a component A and a component B wherein the component A comprises an acid-treated wollastonite compound, an acid aqueous solution of metal phosphate, and a setting retarder; and component B comprises a setting accelerator.		

IMPROVED CEMENT COMPOSITION

The present invention concerns the field of cement, and relates particularly to phosphate cements.

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Following abbreviations will be used throughout the text:

US1 = US Patent 3,642,511

US2 = US Patent 4,956,321

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US3 = US Patent 4,375,516

W1 = WO 97/19033

Invention = newly developed invention.

Background information

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US1 discloses a method to treat wollastonite by acid, say sulphuric acid and phosphoric acid, to a degree of pH \leq 4.0. The aim of the treatment is to have a good opacity properties and low abrasiveness resistance, so that the final product, i.e., acid treated wollastonite, can be used as a pigment for paper industry (column 1, line 41-53).

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US2 discloses a method to treat wollastonite by acid, say sulphuric acid, carbonate acid and acetate acid, to a degree that the treated wollastonite has a pH=9-10. The

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treated wollastonite, called surface-pacified wollastonite in US2, may be used as an inert filler, or in the composition of US3. The aim of treating the wollastonite by the acid is to have a "reaction
5 uniformity" of the wollastonite (column 1, line 19-27), so that the reaction, presumably the quick-setting process of the US3, will not be influenced by the different batches and grades of raw material. As a result, the treated wollastonite has a pH=9-10, which is
10 not fundamentally different from that of the untreated wollastonite of pH=9-10.7 (column 2, line 34-39). This is an indication that US2 seeks to keep the reactivity of the US3 composition. As an evidence, Example 4 of US2 shows a setting time of 1 hour, which is considered as
15 quick-setting in an industrial process. We have tested the Example 2 of US2 to examine its setting process, and the result shows that it has a setting time of less than 10 minutes at 20°C (Table 3).

20 W1, our previous invention, discloses a composition comprising an acid metal phosphate solution, a wollastonite compound and an oxy-boron compound as setting retarder. This composition discloses a technique to reduce reactivity of the composition by the setting
25 retarder which results in a long pot life. The wollastonite used in the W1 is an untreated wollastonite

having a pH = 9-12. The W1 composition may provide a long pot life. However, its setting will take long time as well at 20°C because the reactivity of the composition is significantly reduced by the retarder. High
5 temperature curing may be used to accelerate the setting, but there are times when high temperatures are not suitable.

There is a pressing need to develop a technique to
10 accelerate setting reaction of a composition according to W1, using means other than increased curing temperature, so that a shaped body can be fully cured and obtained in a relatively short period.

15 It is an object of the present invention to provide a composition which fulfils the above need.

Description of the Invention

20 The Invention disclosed herein relates to a phosphate cement composition, its method of preparation and resulting products formed therefrom.

Some particular objectives of the Invention are: (1) to
25 reduce pH value of the wollastonite by a treatment so that reactivity of the said component A can be

fundamentally reduced, resulting in further extended pot life; and (2) to provide a technique so that setting of the composition become obtainable whenever it is required.

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According to one aspect of the present invention there is provided a phosphate cement composition which comprises, in combination, a component A and a component B wherein the component A comprises an acid-treated
10 wollastonite compound, an acid aqueous solution of metal phosphate, and a setting retarder; and component B comprises a setting accelerator.

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Preferably the metal phosphate is selected from the group consisting of: aluminium phosphates, zirconium phosphates, magnesium phosphates, zinc phosphates, calcium phosphates, iron phosphates, including derivatives and mixtures thereof.

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The setting retarder may be selected from the group consisting of boric acid, alkali metal and, alkaline-earth metal salts of boric acid, amine and ammonium salts of boric acid, including hydrates and mixtures thereof.

25

The setting retarder may be selected from the group

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consisting of: boric acid, sodium borate, ammonium borate, calcium borate, including hydrates and mixtures thereof. Preferably said setting retarder is added as a powder or a liquid. Suitable accelerators are known in the art; one is MgO .

The wollastonite of the said acid-treated wollastonite compound may be a natural or synthetic wollastonite, in calcined or non-calcined state, or a combination thereof.

The acid-treated wollastonite has preferably a pH value of 6-8 as measured using a wollastonite 10 % water slurry.

The said acid used to treat the wollastonite may be an inorganic acid. For example, the acid used to treat the wollastonite may be sulphuric acid, phosphoric acid, carbonate acid, acetate acid, or a combination thereof.

According to another aspect of the invention there is provided a method of producing acid-treated wollastonite for a cement composition comprising: (1) mixing wollastonite with an inorganic acid aqueous solution in a concentration and quantity sufficient to form an acid/wollastonite mixture having a $pH=6-8$; and (2) drying

the mixture after its pH value becomes stable.

The said acid may be sulphuric acid, phosphoric acid, carbonate acid, acetate acid, boric acid, or a
5 combination thereof. The said acid preferably has a normality of 0.03 - 0.05.

According to yet another aspect of the invention there is provided a shaped product formed from cement as
10 hereinbefore described.

According to yet a further aspect of the invention there is provided a shaped product containing the acid treated wollastonite as hereinbefore described.

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According to yet another aspect of the invention there is provided a method of making a solid shaped article comprising: providing composition A, forming the composition into a shape, and adding composition C to set
20 the cement in the shape.

In general, the component A has a sufficiently long pot life, while the component B can be added to component at any moment during the pot life to form the cement which
25 sets in relative short period so that a shaped body can be fully cured and produced at circa 20°C by the

Invention.

In general, reducing reactivity of the composition A of the Invention is achieved by treating the wollastonite with acid, to a degree that the treated wollastonite has a pH = 6-8 in wollastonite 10 % water slurry (this method of pH measurement will be used hereafter). When this treated wollastonite of pH = 6-8 meets acid metal phosphate solution, it reacts much slower than that of untreated wollastonite having a pH = 9-12. This results in a more extended pot life for the component A, even compared to that of W1.

On the other hand, controlling the setting time is realised using a setting accelerator. When this setting accelerator is added to the Invention composition A at any moment during the pot life, a setting mechanism is induced immediately which causes setting and full curing of the Invention composition at ambient temperature condition in a relatively short period.

These techniques have never been developed prior to this Invention, specially for the accelerator. This is because the phosphate cement using wollastonite as primary material has always been known as a quick-setting cement (with the exception of that disclosed in W1) so no

setting accelerator has ever been considered necessary.

Following is a description of some comparative tests illustrating the effectiveness of the compositions of the present invention.

Composition

With respect to composition, the Invention is fundamentally different from the W1 (Table 1) in the particular wollastonite employed and presence of the setting accelerator. This significantly improves industrial applicability of the technology.

Compared to US2, the composition of the Invention is evidently different not only in the presence of setting retarder and a setting accelerator, but also in the particular wollastonite employed. The Invention wollastonite is a mixture of a calcium salt of the particular acid used in the treatment (calcium sulphate, for instance), a silica gel and an un-reacted wollastonite, characterised by pH = 6-8. The presence of silica gel indicates that wollastonite structure is attacked during the treatment. While the US2 wollastonite is only surface-pacified with a surface-displaceable anion without altering crystal structure, and having a

pH = 9-10 (column 3, line 30-38). These therefore are two different materials, to be used for different applications.

5 **Table 1 Composition difference**

Invention	W1	US2
as material composition	as material composition	1. as method to treat wollastonite 2. to be used in US3 or as inert filler
acid treated wollastonite pH = 6 to 8	wollastonite compound pH = 9 to 12	acid treated wollastonite pH = 9 to 10
metal phosphate	metal phosphate	metal phosphate
oxy-boron compound	oxy-boron compound	--
setting accelerator	--	--

Setting process

Because of the difference in material composition, setting process of the Invention, US2 and W1 are consequently different, as summarised in the Table 2.

Table 2 Difference in the setting process

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	quick-setting	controlled pot-life	controlled setting time
US2	uncontrollable quick setting		
W1	No	Yes	--
5 Invention	controllable quick-setting*	Yes	Yes

*Controllable quick setting in the sense that the setting can be realised by adding setting accelerator.

10 Comparative tests

Comparative tests has been made, using compositions of the Invention, W1 and US2 to verify their setting process (Table 3). The wollastonite used in the test is very
 15 reactive and has a pH=12. The surface-pacified wollastonite used for US2 is obtained by treating it with sulphuric acid having a normality of 0.01, rinsed with de-ionised water and then dried, as required by the Example 2, US2 (column 3, Example 2). The acid treated
 20 wollastonite used in the Invention is a mixture comprising calcium sulphate, silica gel and un-reacted wollastonite obtained by treating it with sulphuric acid

having a normality of 0.04 and then dried at 60°C.

Table 3 Pot life at 20°C

	-	W1	US2	Invention
5	-	wollastonite	wollastonite	wollastonite
	-	as supplied pH=12	surface- pacified pH=9	acid treated pH=7
	-	min.	min.	min.
	-			
10	phosphate W1 ratio = 1.4(1)	pot life =30, set=45	--	pot life = 180 (2), set=24 hours
	phosphate (3) ratio = 1.4	foaming setting < 10 min.	foaming, setting < 10 min.	foaming, setting < 10 min.

(1) phosphate to wollastonite ratio

15 (2) maximum pot life, no setting accelerator is used

(3) aluminium phosphate from US2 Example 2, columns 3-4.

The test results show that when the US2 composition is used, it is always quick-setting together with foaming,
20 independent of the pH value of the wollastonite. It demonstrates that the surface-pacified wollastonite cannot provide long pot life. On the other hand, when the

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Invention composition is employed, the wollastonite of pH = 7 does reduce reactivity of the component A compared to W1 and the US2, indicated by the dramatic increase of pot life.

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Field of Application

The field of application and industrial applicability is summarised in the table 4.

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Table 4 properties and field of application

-	Field of application	Industrial suitability
Invention	1. fibre reinforced composites 3. cement 4. adhesive 5. foams	much improved over W1
W1	1. fibre reinforced composites 3. cement 4. adhesive 5. foams	Yes
US2	1. foams 2. quick-setting applications	difficult

15

In view of the difference in composition, setting process and industrial applicability, the Invention has novelty. inventive step and industrial applicability with regard to its composition, method of treating the wollastonite
5 and the resulting products formed from the cement.

CLAIMS

1. A phosphate cement composition which comprises, in combination, a component A and a component B wherein the component A comprises an acid-treated wollastonite compound, an acid aqueous solution of metal phosphate, and a setting retarder; and component B comprises a setting accelerator.
2. A phosphate cement composition according to claim 1 wherein the metal phosphate is selected from the group consisting of: aluminium phosphates, zirconium phosphates, magnesium phosphates, zinc phosphates, calcium phosphates, iron phosphates, including derivatives and mixtures thereof.
3. A phosphate cement composition according to claim 1 or claim 2 wherein said setting retarder is selected from the group consisting of boric acid, alkali metal and, alkaline-earth metal salts of boric acid, amine and ammonium salts of boric acid, including hydrates and mixtures thereof.
4. A phosphate cement composition according to claim 3 wherein the setting retarder is selected from the group consisting of: boric acid, sodium borate, ammonium

borate, calcium borate, including hydrates and mixtures thereof.

5 5. A phosphate cement composition according to claim 3 or claim 4 wherein said setting retarder is added as a powder or a liquid.

10 6. A phosphate cement composition according to claim 1 wherein the wollastonite of the said acid-treated wollastonite compound is a natural or synthetic wollastonite, in calcined or non-calcined state, or a combination thereof.

15 7. A phosphate cement composition according to claim 1 and claim 6 wherein said acid-treated wollastonite has a pH value of 6-8 as measured using a wollastonite 10 % water slurry.

20 8. A phosphate cement composition according to claim 1 and claims 6 or 7 wherein the said acid used to treat the wollastonite is an inorganic acid.

25 9. A phosphate cement composition according to claim 1 and any of claims 6 to 8 wherein the acid used to treat the wollastonite is sulphuric acid, phosphoric acid, carbonate acid, acetate acid, or a combination thereof.

10. A method of producing acid-treated wollastonite for a cement composition comprising: (1) mixing wollastonite with an inorganic acid aqueous solution in a concentration and quantity sufficient to form an acid/wollastonite mixture having a pH=6-8; and (2) drying the mixture after its pH value becomes stable.
11. A method according to claim 10 wherein the said acid is sulphuric acid, phosphoric acid, carbonate acid, acetate acid, boric acid, or a combination thereof.
12. A method according to claim 10 or 11 wherein the said acid has a normality of 0.03 - 0.05.
13. A shaped product formed from cement according to any of claims 1-10.
14. A shaped product containing the acid treated wollastonite of claim 11 or 12.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/BE 99/00130

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B28/34 C04B20/02 C04B40/06 //(C04B28/34,14:04,22:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 97 19033 A (VRIJE UNIVERSITEIT BRUSSEL) 29 May 1997 (1997-05-29) cited in the application claims 1-6 ---	1-6,13
A	WO 96 38394 A (RESLAB A/S) 5 December 1996 (1996-12-05) claim 1 ---	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

9 February 2000

Date of mailing of the international search report

16/02/2000

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PCT/BE 99/00130

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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